Parameters for the Identification of Localized Corrosion: Theoretical Analysis

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A number of parameters have been used for the identification of localized corrosion, but despite this, many workers find that the visual examination of the current and potential noise time records remains the most reliable (if not the most cost-effective) technique for this purpose. This paper will examine the techniques that have been used from a theoretical perspective, supplemented by the application of the techniques to simulated and real data.

Characteristics of Localized Corrosion

The term “localized corrosion” refers to a range of corrosion processes, and it is not realistic to expect all of them to have comparable electrochemical characteristics. However, for practical corrosion monitoring applications it is reasonable to consider a sub-set of localized corrosion processes that includes pitting corrosion, crevice corrosion and stress corrosion cracking. These are characterized by relatively low frequency, large amplitude current and potential ‘events’. Thus human analysts generally take large amplitude events occurring simultaneously in both the potential and current time record as indicative of localized corrosion. They will usually also take account of the sign of the events where it is relevant. Thus potential events, when measured with respect to a stable reference electrode, should generally be negative-going, corresponding to activation of one or other of the two working electrodes. Consequently positive-going events can usually be dismissed as extraneous interference. If the reference electrode is of the same material as the working electrodes, then positive-going events would correspond to activation of the reference electrode, and would not be expected to be accompanied by a current event.

The Coefficient of Variation of Current

This is defined as the standard deviation of current divided by absolute value of the mean current. At first sight the expected value of the mean is zero, so the expected value of the coefficient of variation is infinity. However, the absolute value operation changes this, and the expected value of the mean is related to the standard error of the estimate of the mean, and it turns out that the expected value of the coefficient of variation is proportional only to the square root of the number of samples in the time record, and this is demonstrated by simulation results. In real systems the two current measuring electrodes are typically not similar, and the coefficient of variation is strongly dependent on the asymmetry between the two electrodes.

The Localization Index

The localization index is defined as the standard deviation of current divided by the rms current. Since the rms current is always greater than or equal to the standard deviation, this can never exceed 1, and therefore avoids the problems of the coefficient of variation when the mean happens to be zero. However, there is a direct relationship between the two parameters, and the expected value of the localization index for perfectly symmetrical electrodes is very close to 1.

Skew and Kurtosis

Skew describes the distortion of the symmetry of a distribution with respect to the normal distribution, while kurtosis describes the flatness or peakedness. For relatively infrequent events it is clear that ‘one-sided’ events (such as activation events in the potential noise) will give a non-zero skew, while two-sided events (such as the current noise between two active electrodes) will give zero skew, but a non-zero normalized kurtosis. As the frequency of events increases, it is an inevitable result of the central limit theorem that the distributions will tend towards normal, and the skew and kurtosis will both tend to zero.

Characteristic Charge and Frequency

An analysis based on shot noise theory, and assuming the validity of determining corrosion current density from the noise resistance, enables the estimation of the average charge in the individual events and the frequency of those events. Localized corrosion may then be identified as having a low frequency of events, while the charge is an indication of the intensity of the process. It is less clear what these parameters mean for processes that do not strictly have the characteristics of shot noise, and further work is needed to test them in real systems.

Spectral Analysis

Current and potential power spectra have been widely used as descriptors of the properties of noise time records, and features such as the roll-off slope at higher frequencies and the knee frequency have been correlated with the type of corrosion. Theoretical analyses show that the shape of a power spectrum produced from the sum of a number of events is the same as that for the individual event. Consequently the only evidence in power spectra that relates to the frequency or amplitude of the events is present in the amplitude of the spectra, not the shape.

Future Developments

The various techniques that are available are potentially able to extract some of the information derived by a human analyst, notably the amplitude and frequency of events occurring. Few techniques take account of the correlation in time between current and potential events or of the directionality of events. As these are key features used by human analysts to interpret and to validate the data, it seems probable that future developments will take these features into account, possibly by using cross-correlation and similar methods.